Effects of AlO Addition on Glassy Phase Separation and Crystallization of a PbO-TiO-SiO Glass

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CITATION:

Kokubo, Tadashi ...[et al]. Effects of AlO Addition on Glassy Phase Separation and Crystallization of a PbO-TiO-SiO Glass. Bulletin of the Institute for Chemical Research, Kyoto University 1973, 50(6): 608-620

ISSUE DATE:

1973-03-15

URL:

http://hdl.handle.net/2433/76464

Bull. Inst. Chem. Res., Kyoto Univ., Vol. 50, No. 6, 1972

Effects of Al_2O_3 Addition on Glassy Phase Separation and Crystallization of a PbO-TiO_2-SiO_2 Glass

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Received October 24, 1972

The crystallization processes of the PbO 40, TiO_2 25, SiO_2 35 mole % glass and PbO 40, TiO_2 25, Al_2O_3 10, SiO_2 25 mole % glass were investigated in detail by DTA, electrical resistivity measurement, X-ray diffraction analysis, electron microscopic observation, infrared spectroscopic analysis and fluorescent X-ray spectroscopic analysis. It was found that the former crystallizes directly forming a metastable pyrochlore-type lead titanate, whereas the latter forms the perovskite-type $PbTiO_3$ crystals via a glassy two-phase separation. It is concluded that addition of the Al_2O_3 to a PbO-TiO_2-SiO_2 glass induces a glassy two-phase separation, and as the result promotes precipitation of the perovskite-type $PbTiO_3$ crystal, thus suppressing formation of the metastable crystal.

I. INTRODUCTION

Some glasses in the PbO-TiO_2-SiO_2 system convert into polycrystalline aggregates consisting mainly of perovskite-type $PbTiO_3$ crystals with high dielectric constants on their heating[1~7]. A composition region in the PbO-TiO_2-SiO_2 system from which the perovskite-type $PbTiO_3$ crystals precipitate as an initial phase is narrow, but can be expanded to some extent by addition of Al_2O_3; the Al_2O_3 enhances the precipitation of the perovskite-type $PbTiO_3$ crystals probably by suppressing formation of metastable pyrochlore-type lead titanates which usually tend to precipitate in the PbO-TiO_2-SiO_2 compositions.[6]

In the present study, in order to provide a more sound experimental basis for reasoning the effect of the Al_2O_3 addition in enhancing the precipitation of the perovskite-type $PbTiO_3$, the effects of the Al_2O_3 addition on the crystallization process of a PbO-TiO_2-SiO_2 glass has been investigated in detail. Previous works dealing with crystallization process of the PbO-TiO_2-SiO_2 glasses are few and fragmental in content especially as to effects of addition of the Al_2O_3; Martin[4] found formation of the pyrochlore-type lead titanate crystals in PbO-TiO_2-SiO_2-(B_2O_3 or Na_2O) glasses on their heating. Russell *et al*[2,3] found development of a two-liquid phase separation in the PbO 34.7, TiO_2 17.3, Al_2O_3 10.9, SiO_2 37.1 (by mole %) glass on its heating prior to precipitation of the perovskite-type $PbTiO_3$ crystals. In both reports, however, no explanation was made of the effects of addition of the Al_2O_3.

II. EXPERIMENTAL

1. Glass Preparation

Two glasses of the compositions, PbO 40, TiO_2 25, SiO_2 35 (glass 1) and PbO 40,

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TiO_2 25, Al_2O_3 10, SiO_2 25 (glass 2) by mole % were prepared. The batch materials used were red lead, titanium oxide and aluminum hydroxide, all of reagend grade, and acid-washed pure quartz powders for manufacturing optical glasses. The batches of approximately 100 g in quantity were put in a Pt10Rh crucible covered with a lid and melted in a SiC furnace at 1250°C for 30 min. The melts were poured on a steel plate, crushed to −100 mesh and remelted at 1250°C for 30 min. The melts were then cast in a graphite mold into a form of disc 3 cm in diameter and 3 mm thick. The casts were heated to 500°C in an electric furnace, and then, after the electric current was cut off, they were allowed to cool in the furnace.

2. Dynamic Analysis of Crystallization Process

2.1 Differential Thermal Analysis

The annealed glass discs were partly cut into cylindrical pieces, 9 mm in diameter and 12 mm in length, so that they fit to a hole of the sample holder of the DTA apparatus (Type DT-10B, Shimazu Seisakusho Ltd.). The DTA were made at a heating rate of 2°C/min. Alpha-Al_2O_3 powder was used as a reference.

The thermograms obtained for each glasses are shown in Fig. 1. Glass 1 shows an endotherm at 530°C and an exotherm at 630°C, whereas glass 2 shows an endotherm at 570°C and two exotherms at 620° and 640°C.

2.2 Electrical Resistivity Measurement during Heat-Treatment

The annealed glass discs were ground flat and finished with 2000 grade alumina powders. Their final thickness was about 2 mm. After gold electrodes were vacuum-evaporated on the discs with a guard ring annulus on one side, they were placed in a nickel-chrome steel (NAS-20) sample holder, and heated at a rate of 1.3°C/min in a nichrome-wounded furnace, as schematically shown in Fig. 2. During the heating, the resistivities were measured under an alternative field at a frequency of 30 c/sec for preventing electrode

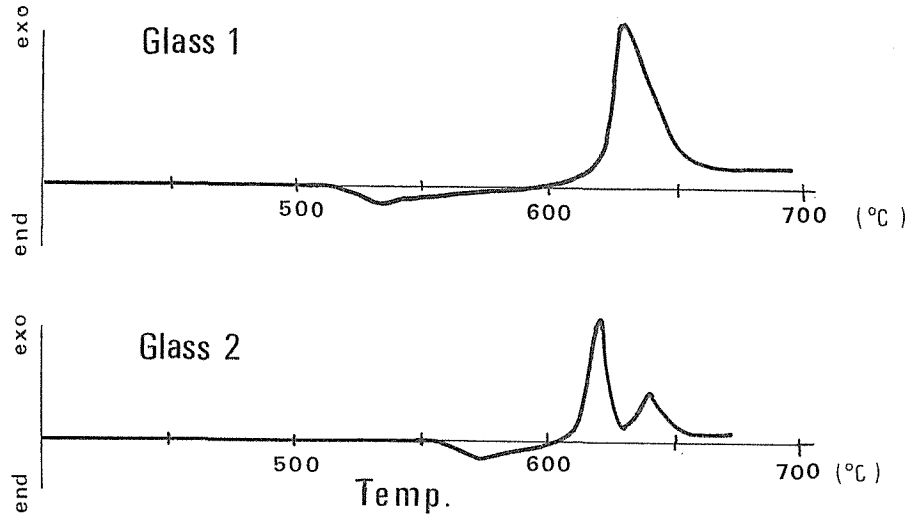


Fig. 1. Differential thermal analysis curves

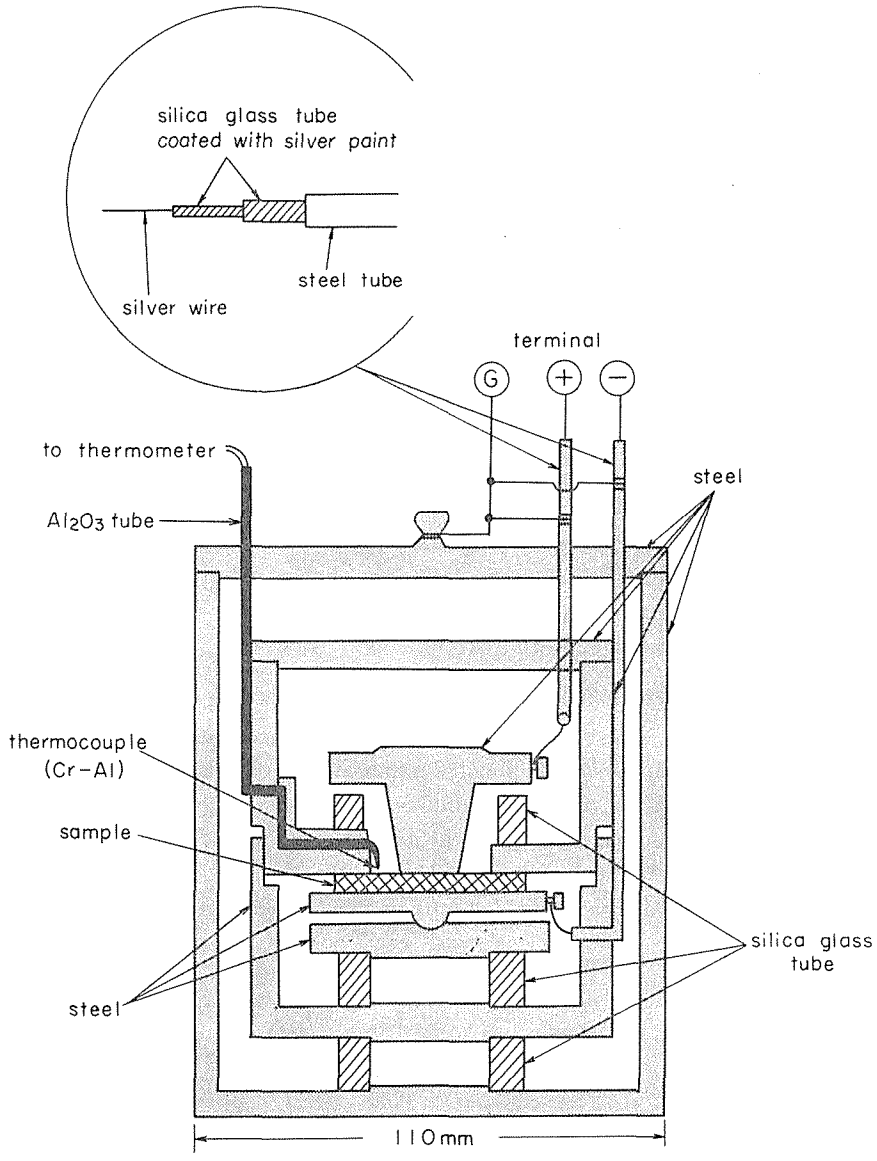


Fig. 2. Sample cell for measurement of electrical properties.

polarization, using a transformers bridge (Type TRS-B, Ando Electric Co. Ltd.).

The results are shown in Fig. 3. Glass 1 exhibits an inflection at approximately 540°C and a minimum at 620°C in its resistivity versus temperature curve, whereas glass 2 exhibits an inflection at 560°C and two minima at 610° and 620°C. These inflections and minima corresponded nearly to the temperatures of the endotherm and exotherms for each glass, although their exact correlation was difficult because of the difference in the heating rate between the resistivity measurement and DTA.

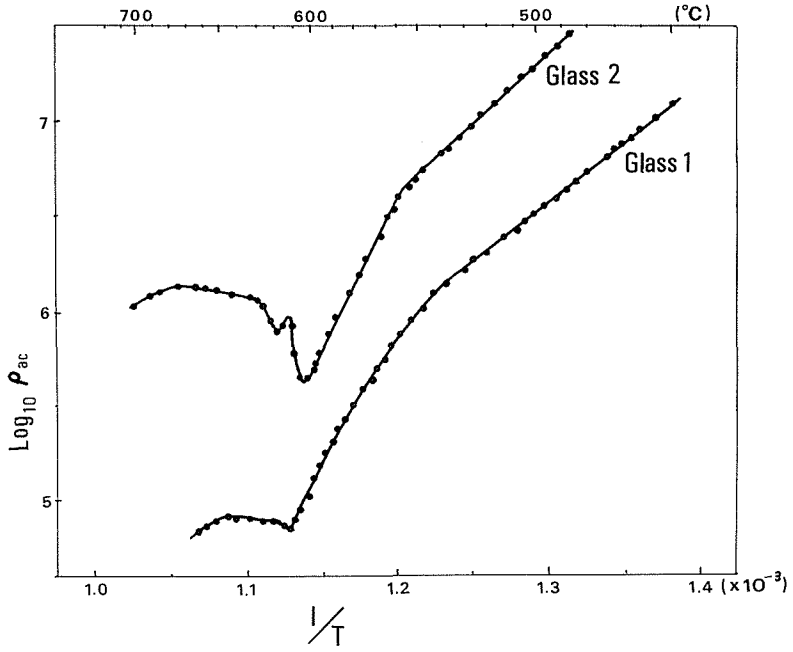


Fig. 3. Log_{10} (resistivity) at 30 c/s *vs.* reciprocal absolute temperature.

3. Static Analysis of Crytallization Process

The foregoing dynamic analyses suggest structural changes at 530°–540°C and 620°–630°C in glass 1, and at 560°–570°C, 610°–620°C and 620°–640°C in glass 2. In order to investigate these changes, the glasses as-annealed and heated, at a rate of 1.3°C/min, to various temperatures below and above these temperatures were subjected to the following analyses.

3.1. X-Ray Diffraction Analysis

For glass 1, no crystal was found in any of the specimens heated up to temperatures below 600°C whereas the crystals reported by Martin[4] as a pyrochlore-type lead titanate were found in the specimen heated up to 630°C. This titanate was found to be transformed into the perovskite-type $PbTiO_3$ crystal near 700°C. For glass 2, no crystal was found in any of the specimens heated up to temperatures below 615°C whereas the perovskite-type $PbTiO_3$ crystals were found in the specimens heated up to temperatures above 625°C.

3.2 Electron Microscopic Observation

The fracture surfaces of the specimens were etched with 10% HCl and replicated with carbon film shadowed by platinum-palladium. Some of the electron micrographs of the replicas are shown in Fig. 4, from which the following structural changes can be seen: glass 1 as-annealed has a uniform structure but, when heated to 630°C, forms a large number of irregularly-shaped particles approximately 5000 Å in size. On the contrary, for glass 2 a large number of tiny particles 200 to 500 Å in diameter are observed even in the specimen as-annealed. These particles grow to a few thousand angström in diameter on heating to 615°C, and on futher heating to 625°C, their forms change from

fairly round to irregular while their size remains almost unchanged.

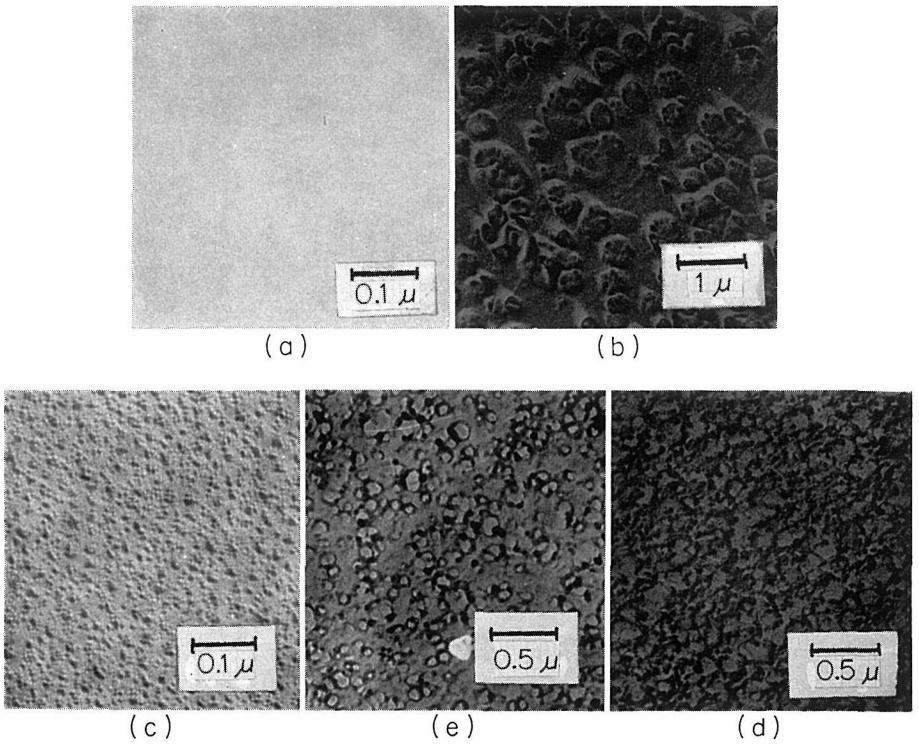
3.3 Electrical Resistivity Measurement

The d.c. resistivities at temperatures 200° to 300°C were measured of the as-annealed and heat-treated glasses with a Teraohmmeter (Type RM-21, Yokogawa Electric Works Ltd.).

The results are shown in Fig. 5, which indicates that for both glasses 1 and 2, the d.c. resistivities at 200° to 300°C remain unchanged when the maximum temperatures of their heat treatment are below those corresponding to the minima of their a.c. resistivities, *i.e.* 620°C for glass 1 and 610°C for glass 2, whereas once they are heat-treated over those temperatures the d.c. resistivities increase. Activation energies for d.c. conduction obtained from the data shown in Fig. 5 were almost constant irrespective of the temperature of the preceding heat treatment for each glass; 27 Kcal/mole for glass 1 and 30 Kcal/mole for glass 2.

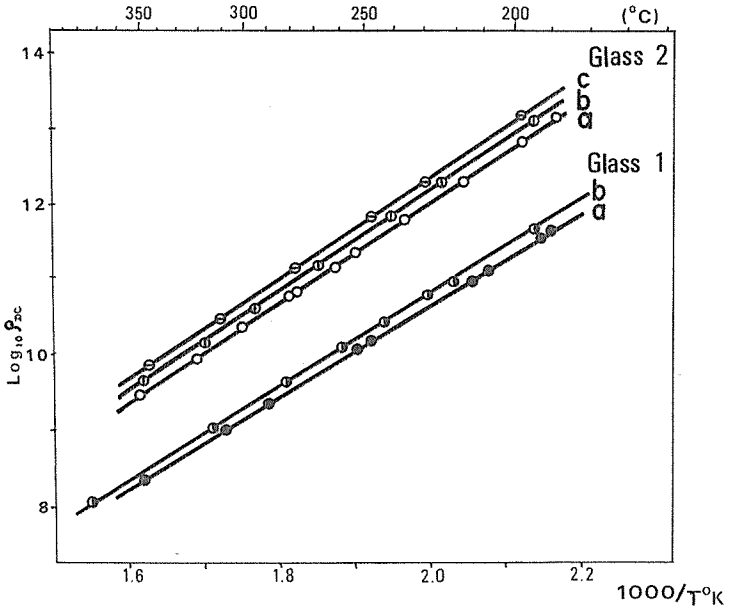
3.4 Infrared Spectroscopic Analysis

The infrared absorptions of the glasses 1 and 2 were measured with a double-beam



(a) Glass 1 as-annealed
(b) Glass 1 heated to 630°C.
(c) Glass 2 as-annealed
(d) Glass 2 heated to 615°C.
(e) Glass 2 heated to 625°C.

Fig. 4. Electron micrographs of glasses



Glass 1 (a) as-annealed and heated to 600°C
(b) heated to 630°C
Glass 2 (a) as-annealed and heated to 600°C
(b) heated to 615°C
(c) heated to 625°C

Fig. 5. Effect of heat-treatment on d. c. resistivity

automatic infrared spectrometer (Perkin-Elmer 521) by a KBr disc method. As references, those of two glasses of the compositions PbO 50, SiO_2 50, and PbO 47.5, TiO_2 47.5, SiO_2 5 by mole %, of which the latter was prepared by "splat quenching" method[8], as well as three crystalline powders of PbO, Pb_3O_4 and perovskite-type tetragonal $PbTiO_3$ were used.

The results are shown in Fig. 6. In the spectrum of as-annealed glass 1, broard bands are observed near 925, 730, 600 and 470 cm^{-1}. On heating to 630°C, a sharp peak at 1045 cm^{-1} newly appears and the intensity of the absorption near 800–600 cm^{-1} decreases whereas that near 600–400 cm^{-1} increases.

In the spectrum of as-annealed glass 2, broad bands are observed near 950, 630 and 470 cm^{-1}. On heating to 615°C and then to 625°C, the band near 950 cm^{-1} shifts to higher frequencies, and at 625°C the absorptions near 570 and 350 cm^{-1} increase their intensities.

3.5 Fluorescent X-Ray Spectroscopic Analysis

In order to determine the coordination number of the Al atom to the oxygen atoms, as-annealed and heat-treated glasses 2 were subjected to the fluorescent X-ray spectroscopic analyses, using α-Al_2O_3 powder as a standard material containing six-fold coordinated aluminum, and K-feldspar and Na-feldspar as those containing four-fold coordinated aluminum. The fluorescent X-ray spectra were registered with a automatic fluorescent

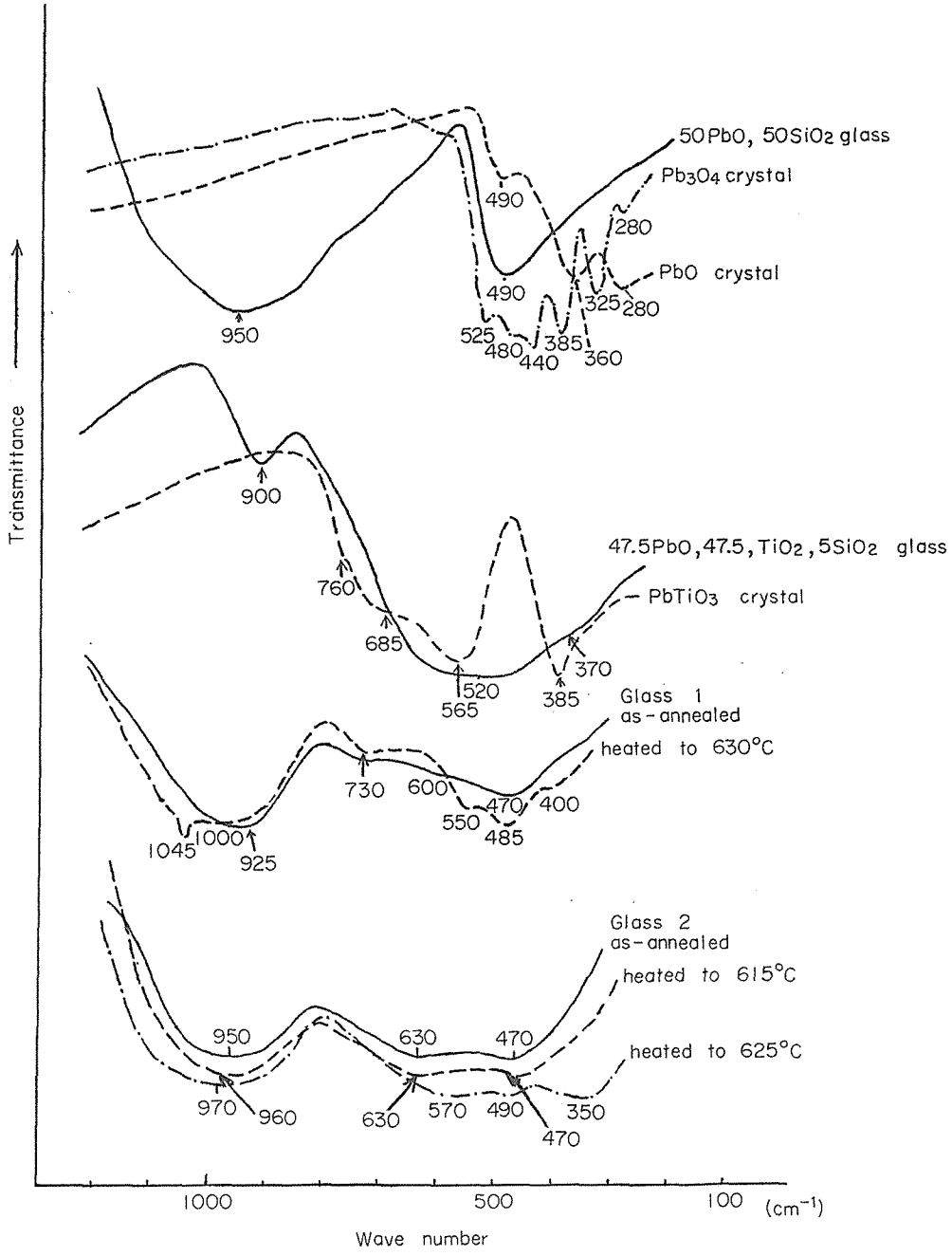


Fig. 6. Infrared spectra of crystals and glasses

X-ray spectrometer (Geigerflex KG-4, Rigaku Denki Kogyo Co., Ltd.) on the following conditions;

X-ray tube: Cr target, Applied field: 50 KV
Tube current: 40 mA, Detector: Gas flow proportional counter

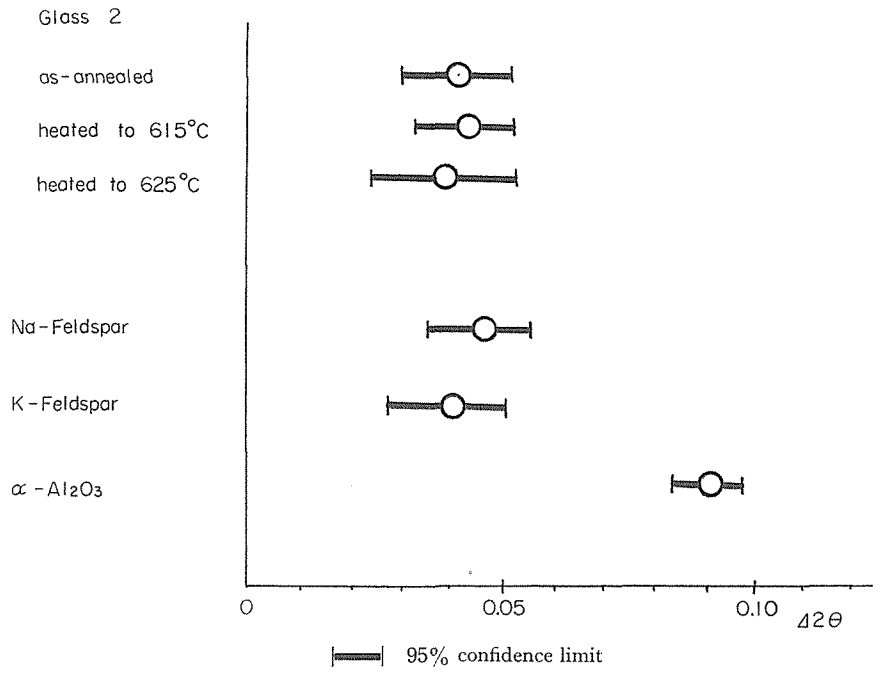


Fig. 7. Graphical representation of $\Delta 2\Theta$, difference in diffraction angle of Al-Kα radiation between Al metal and Al ion in various minerals and glass 2.

Pulse height analyzer: Differential,
Monochromator crystal: EDDT (2d=8.808 Å)
Dispersion angle of solar slit: 0.15°
X-ray path: Vacuum (10^{-1}—10^{-2} mmHg)
Temperature: 29.0±1.0°C

Positions of Al-$K\alpha$ peaks measured at 90%-maximum intensity are shown of the glasses and the standard materials in Fig. 7. They were represented in terms of displacement from that of the aluminum metal measured together. The positions of Al-$K\alpha$ peaks for glasses 2 almost agree, irrespective of heat treatment, with those of K- and Na-feldspars both containing four-fold coordinated Al atoms.

III. DISCUSSION

1. Crytallization Process of Glass 1

The electron micrograph indicates that as-annealed glass 1 is homogeneous. The endotherm and the inflection in the a.c. resistivity found at 530°–540°C is considered to be indications of glass transformation, because no change in structure was detected by any of the static analyses made for the specimens once heated to or a little over this temperature. As confirmed by X-ray diffraction analysis, precipitation of the pyrochlore-type lead titanate crystals from this glass occurs at 620°–630°C, being accompanied by the

exotherm and the increase in the a.c. resistivity. The fact that no change in the structure was detected by any of the static analyses made for the specimens once heated to a little below this crystallization temperature futher leads to a conclusion that the crystals precipitate directly from the homogeneous glass, without precursory structural change in the mother glass such as glassy two-phase separation.

A deeper insight into change in the internal structure of the glass on heating can be gained from its infrared absorption studies: First, consider coordinations of Si^{4+}, Ti^{4+} and Pb^{2+} ions in as-annealed glass 1. For a large number of silicate glasses, the absorption band characteristic of Si-O stretching vibrations is observed at a frequency of 900–1100 cm^{-1}.[9] The band near 925 cm^{-1} found in the spectrum of as-annealed glass 1 is, therefore, assigned to this vibrations. This is also supported by the fact that such a band is also found in those of the SiO_2-containing oxides such as the PbO-SiO_2, PbO-TiO_2-SiO_2 and PbO-TiO_2-Al_2O_3-SiO_2 glasses, but not in those of the PbO, Pb_3O_4 and $PbTiO_3$ crystals. The frequency value of this band, 925 cm^{-1}, due to the Si-O stretching vibrations, however, is rather low in comparison with that of the PbO 50, SiO_2 50 glass examined in the present work as well as those of the other silicate glasses.[9,10] Since the frequency of the band due to the Si-O stretching vibrations generally decreases as SiO_4 tetrahedra become isolated,[9,10] the above fact indicates that the SiO_4 tetrahedra in as-annealed glass 1 are fairly uniformly distributed in an isolated state. This is consistent with the result of the electron microscopic study that the glass 1 as-annealed and heated to temperatures a little below the crystallization temperature was not separated into two-glassy phases but homogeneous. The absorption bands characteristic of the Ti-O stretching vibrations in four-fold coordination and six-fold coordination are generally located at 800–690 and 650–500 cm^{-1}, respectively.[9] In fact, such bands were observed for the TiO_2-containing oxides such as the $PbTiO_3$ crystal, the PbO-TiO_2-SiO_2 and PbO-TiO_2-Al_2O_3-SiO_2 glasses, but not for the PbO crystal, the Pb_3O_4 crystal and the PbO-SiO_2 glass. The bands near 730 and 600 cm^{-1} in the spectrum of as-annealed glass 1 are, therefore, attributed to the Ti-O stretching vibrations in the four-fold and six-fold coordination, respectively. It is known that TiO_4 tetrahedra can replace SiO_4 tetrahedra[11] and Pb^{2+} ions, forming PbO_4 tetrahedra, also enter into glass networks, especially when the PbO content is high.[12,13] In as-annealed glass 1, therefore, SiO_4, TiO_4 and PbO_4 tetrahedra may be fairly uniformly distributed, forming a glass network, while the remaining Ti^{4+} and Pb^{2+} ions may sit in holes in the network as modifiers.

Infrared spectrum of glass 1 heated to 630°C affords an insight into the structure of the pyrochlore-type lead titanate precipitating in the glass. In comparison with the spectrum of as-annealed glass 1, that of glass 1 heated to 630°C has a stronger absorption band at 600–500 cm^{-1} characteristic of TiO_6 octahedra and a new sharp peak at 1045 cm^{-1} characteristic of SiO_4 tetrahedra in crystals respectively. This result is in good accordance with the model of the pyrochlore-type lead titanate presented by Martin[4] that the crystal is composed essentially of PbO_6 and TiO_6 octahedra and in addition a small amount of SiO_4 tetrahedra.

2. Crystallization Process of Glass 2

The electron microscopic observation shows that as-annealed glass 2 is already separated into two glassy phases; glassy droplets 200 to 500 Å in diameter and continuous

glassy matrix. Since the $PbTiO_3$ crystals appear to precipitate in the droplet phase at the final stage of the heating as described later in detail, it is probable that the droplets are enriched with PbO and TiO_2 whereas the matrix is enriched with SiO_2. The enrichment with SiO_2 is also indicated by the heigher frequency of the infrared absorption band due to the Si-O stretching vibrations for as-annealed glass 2 than that for as-annealed glass 1; *i.e.,* 950 cm^{-1} for glass 2 whereas 925 cm^{-1} for glass 1. The infrared spectrum also indicates that much of the titanium ions condensed in the droplets are in six-fold coordination because the absorption near 630 cm^{-1} for as-annealed glass 2 is much stronger than that for as-annealed glass 1. It should be noted that this coordination number is the same as that of the Ti^{4+} ions in the perovskite-type $PbTiO_3$ crystals precipitating at the later stage.

On heating, glass 2 undergoes glass-transformation at 560°–570°C as indicated by the endotherm and the inflection in the a.c. resistivity. The exotherm and the sudden increase in the a.c. resistivity at 610°–620°C is ascribed to a rapid progress of glassy two-phase separation because in the glass heated to 615°C no crystal was detected by the X-ray diffraction analysis but big glassy droplets were found by the electron microscopic analysis. These big droplets may be considered to have been produced by marked growth of the minute glassy droplets which pre-existed in the glass as-annealed but not by their coalescence, because the growth is accompanied by an irreversible increase in the electric resistivity. If so, the glassy two-phase separation at 610°–620°C would accelerate concentration of SiO_2 in the continuous matrix phase. In fact, the infrared spectroscopic analyses show that the Si-O stretching vibration of near 950 cm^{-1} shifts to higher frequency on heating to 615°C.

The exotherm and the increase in the a.c. resistivity at 620°–640°C are ascribed to precipitation of the perovskite-type $PbTiO_3$ crystals as indicated by the X-ray analysis. The $PbTiO_3$ crystals appear to precipitate in the glassy droplets because the grain size and the distribution of the as-separated $PbTiO_3$ crystals were similar to those of the glassy droplets.

A big difference between the crystallization process in glass 1 and 2 is that, as a precursory of the formation of the perovskite-type crystals, the precipitation of the metastable pyrochlore-type lead titanate crystals occurs in glass 1 whereas the glassy two-phase separation occurs in glass 2. Once glassy droplets enriched with PbO and TiO_2 are formed by the glassy two-phase separation, the perovskite-type $PbTiO_3$ crystals would be easy to precipitate in the glassy droplets more or less analogous in composition and hence in structure to those of the crystals. This is probably the reason why the perovskite-type $PbTiO_3$ crystals are precipitated directly from glass 2 without going through any precipitation of metastable crystals. Why the addition of the Al_2O_3 to the PbO-TiO_2-SiO_2 system enhances its glassy two-phase separation will be discussed in the next section.

3. Effects of Addition of Al_2O_3 on Glassy Two-Phase Separation

It is known that addition of the Al_2O_3 to alkaline or alkaline-earth silicate glasses is effective in reducing their tendency toward glassy two-phase separation.[14,15] The addition of the Al_2O_3 to the present PbO-TiO_2-SiO_2 system, however, showed the reversed effect, *i.e.,* its addition rather promoted the phase separation.

The former effect has been attributed by Warren[15] to the ability of the Al^{3+} ion to

replace Si^{4+} ion isomorphously in the glass structure. Later, one of the present authors[16] has presented a more detailed explanation: The phase-separation in oxide glasses arises from the competition among various cations to provide themselves with oxygen ions in accordance with their own coordination number.[17] If the field strength of modifier cation in silicate glasses is higher, these cations tend to cluster to provide themselves with their accompanying polarizable oxygen ions most effectively rather than to stay in their original holes of the silica network. Actually, for example, the Li_2O-SiO_2 and CaO-SiO_2 systems show such a tendency. When the Al_2O_3 is added to these binary systems, the Al^{3+} ion replaces Si^{4+} ion isomorphously and seizes the polarizable singly bonded oxygen ion accompanied with the modifier cations to acheive its four-fold coordination, and thus the phase separation of the system is suppressed.

In order to explain the reversed effect of the Al_2O_3 on the PbO-TiO_2-SiO_2 system, one must take into consideration the fact that in this system there are no typical modifier ions and all the oxygens are accompanied with network-forming or intermediate cations.

The published phase diagram[18] of the TiO_2-SiO_2 system shows a wide stable immiscible region from 20 to 90 mole % TiO_2. This is understandable because both cations in this system have high field strengths; those of Si^{4+} and Ti^{4+} ions are 1.25 and 0.96, respectively, as expressed by $Z_i/(r_i+r_o)^2$, where Z_i is the valency of the cation, and r_i

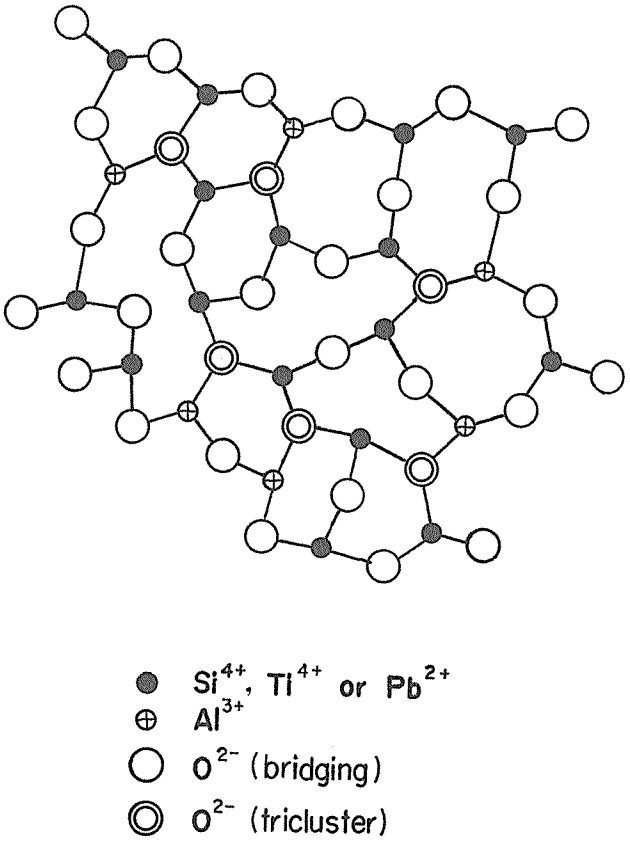


Fig. 8. Two-dimensional structural model of a PbO-TiO_2-Al_2O_3-SiO_2 glass.

and r_O are the ionic radii of the cation and oxygen ion, respectively. When the PbO is added to the TiO_2-SiO_2 system, a tendency toward phase separation will be suppressed because the strong demands of the Si^{4+} and Ti^{4+} ions to be surrounded by polarizable oxygen ions are partly satisfied by the oxygen ions accompanied by the Pb^{2+} ions whose field strength is as low as 0.27. In fact, one of the PbO-TiO_2-SiO_2 glasses, *i.e.*, glass 1, did not show any glassy two-phase separation. When the Al_2O_3 is futher added to the PbO-TiO_2-SiO_2 system, the Al^{3+} ions will replace Si^{4+} ions. In fact, the presence of the Al^{3+} ions coordinated with four oxygen ions in glass 2 has been confirmed by the fluorescent X-ray analyses in the present study. However, since this system contains no alkaline ions and accordingly no singly bonded oxygen the Al^{3+} ions must utilize oxygens already bridging two tetrahedra, as shown in Fig. 8. This type of structural unit, named as "tricluster" because one oxygen is shared with three tetrahedral groups, is well known in some crystals and was first suggested to exist also in some of glasses by Lacy.[19] Since the Al^{3+} ions have a field strength as high as 1.77, the demand of the Al^{3+} ion to be surrounded by oxygen ions would hardly be satisfied by the oxygen ions bridging two Si^{4+} ions with high field strengths. Then the Al^{3+} ions tend to form own phase in which they can find in their vicinity rather polarizable oxygen ions by forming the triclusters with the Pb^{2+} or Ti^{4+} ions. This may be a reason why the Al_2O_3 introduced to the PbO-TiO_2-SiO_2 glass induces the glassy two-phase separation.

IV. SUMMARY

1. It is concluded that the glass of PbO 40, TiO_2 25, SiO_2 35 by mole %, as annealed, has a homogeneous structure being composed of a network of uniformly distributed SiO_4, TiO_4 and PbO_4 tetrahedra and modifier ions of Ti^{4+} and Pb^{2+} sitting in holes in the network. On heat treatment, the glass crystallizes directly forming a metastable pyrochlore-type lead titanate dissolving small amount of SiO_2, without going through any precursory structural change such as glassy two-phase separation. At an elevated temperature, the pyrochlore-type crystals transform to the perovskite-type $PbTiO_3$ crystals.

The glass of PbO 40, TiO_2 25, Al_2O_3 10, SiO_2 25 by mole %, as-annealed, has a two-phase structure being composed of a large number of minute glassy droplets rich in PbO and TiO_2 and a continuous glassy matrix rich in SiO_2. On heat treatment, the droplets first grow in size at the expence of the matrix, so rapidly as a sharp exotherm peak can be observed in DTA, and then the perovskite-type $PbTiO_3$ crystals precipitate in the droplets.

2. It is concluded that addition of the Al_2O_3 to a PbO-TiO_2-SiO_2 glass induces a glassy two-phase separation, and as a result promotes precipitation of the perovskite-type $PbTiO_3$ crystals in the PbO- and TiO_2-rich phase, thus suppressing formation of the metastable crystal. The effect of the Al_2O_3 on the glassy two-phase separation is interpreted in terms of "tricluster" model proposed by Lacy and the field strengths of the constituent ions.

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